

JAPANESE

[JP,2007-056024,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

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[Translation done.]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to the manufacturing method of a norbornene derivative useful as a precursor of an epoxy compound as a radical hardenability compound.

[Background of the Invention]

[0002]

The norbornene derivative is widely used as an additive agent in the technical field of unsaturated polyester for the purpose of the improvement of hardness and toughness or the improvement of the compatibility of unsaturated polyester and styrene (refer to the following patent documents 1). This norbornene derivative is used also as an intermediate at the time of manufacturing a cyclo aliphatic epoxy compound (refer to the following patent documents 2). Functional group content norbornene and the compound which has two or more norbornene structures in molecular structure are especially very useful as said intermediate or an additive agent from the point of excelling in the outstanding compatibility and the above-mentioned mechanical property.

[0003]

These norbornene derivatives are usually industrially produced by the Diels-Alder reaction of a cyclopentadiene and an unsaturated compound.

Specifically, functional group content norbornene is manufactured from the functional group content unsaturated compound and the cyclopentadiene.

For example, norbornene carbaldehyde is manufactured from a cyclopentadiene and an acrolein and norbornene carboxylic acid butylester is manufactured from a cyclopentadiene and butyl acrylate. Cull big ANHIDORIDO is manufactured from the cyclopentadiene and the maleic acid anhydride.

[0004]

In order to attain high conversion in such a Diels-Alder reaction, What is called dienophile needs to be in the state where electron density is low, and, so, it is necessary to have aldehyde, ester, ketone, or an electronic suction nature functional group called an acid anhydride in the molecular structure of this dienophile.

[0005]

On the other hand, when the unsaturation dienophile compound which does not have a functional group of such strong electronic suction nature was used, since it was usually low, the inversion rate of the Diels-Alder reaction needed to react by high temperature service in order to raise yield. For example, the reaction of an allyl ether compound or an allyl alcohol compound, and a cyclopentadiene dimer advances only by high temperature service. Are concrete. A cyclopentadiene dimer is divided in a cyclopentadiene under this high temperature service, and it is the spot and reacts to an allyl ether compound or an allyl alcohol compound. As polyfunctional substances, commercially, since acquisition

was easy, it was [ among these ] very important [ an allyl ether compound, for example, mono- of trimethylolpropane, di-, tri-allyl ether, etc. ] as precursors of a polyfunctional norbornene compound.

[0006]

However, it is necessary to long-time-ize reaction time for reaction temperature more more highly for the reaction of \*\* et al. and said allyl ether compound, and such a reaction condition generates oligomer, such as a trimer of a cyclopentadiene, and a tetramer, so much for it. For example, when a cyclopentadiene dimer is made to react to allyl alcohol, generating a byproduction living thing like the trimer of a cyclopentadiene and a tetramer is known (refer to the following, the patent documents 3, and patent documents 4).

[0007]

Usually, since the boiling point of the trimer of a cyclopentadiene, a tetramer, and an oligomer ingredient was high, they were difficult to dissociate and remove, and the complicated separation method which often starts as for time was required for them. Depending on the by-product, solubility was hardly shown, and there was also a problem of inducing nebula, precipitate, and a smell. In order are serious and to change all the allyl ether functional groups by the case where a polyfunctional norbornene compound is manufactured from polyfunctional allyl ether, the cyclopentadiene needed to be used for such a problem at high concentration within the batch.

[0008]

Therefore, a manufacturing method of the norbornene derivative which can control generation of the trimer of a cyclopentadiene, a tetramer, and an oligomer ingredient, and is obtained by a high grade in the target compound was desired.

[0009]

[Patent documents 1] U.S. Pat. No. 4233432 gazette

[Patent documents 2] U.S. Pat. No. 3187018 gazette

[Patent documents 3] JP,2003-55280,A

[Patent documents 4] JP,2003-55284,A

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0010]

There is the issue which this invention tends to solve in providing the manufacturing method of the norbornene derivative which can manufacture a norbornene derivative by high yield and a high grade by controlling generation of the trimer of a cyclopentadiene, a tetramer, and an oligomer ingredient.

[Means for Solving the Problem]

[0011]

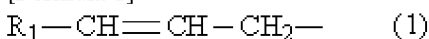
As a result of repeating examination wholeheartedly that an aforementioned problem should be solved, this invention persons by making an allyl compound react to a surprising thing with an alkyl cyclopentadiene dimer, Said technical problem can be solved, this finds out that generation of a trimer of a cyclopentadiene, a tetramer, and an oligomer ingredient can be controlled easily, and it came to complete this invention.

[0012]

Namely, an allyl group as which this invention is expressed in the following structural formula (1)

[0013]

[Formula 1]



[0014]

(R<sub>1</sub> expresses a hydrogen atom, an alkyl group, a hydroxyalkyl group, or an alkoxyalkyl group among a formula, respectively.)

It is related with a manufacturing method of an allyl compound (A) to contain and a norbornene derivative making an alkyl cyclopentadiene dimer (B) react.

[Effect of the Invention]

[0015]

According to this invention, even if it is the same reaction condition as a metaphor compared with the case where it is made to react to the conventional cyclopentadiene dimer, generation of the trimer of a cyclopentadiene, a tetramer, and an oligomer ingredient can be controlled.

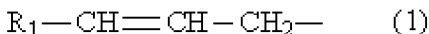
[Best Mode of Carrying Out the Invention]

[0016]

The manufacturing method of this invention makes an alkyl cyclopentadiene dimer (B) react to an allyl compound (A), and is characterized by the allyl compound (A) having the structure expressed with the following structural formula (1) as described above.

[0017]

[Formula 2]



Here,  $R_1$  expresses a hydrogen atom, an alkyl group, a hydroxyalkyl group, or an alkoxyalkyl group, respectively.

[0018]

As for said alkyl group, alkyl groups of C1-C4, such as a methyl group, an ethyl group, a propyl group, or t-butyl group, are mentioned to a hydrocarbon group with 1-4 carbon atoms, and a concrete target. As for a hydroxyalkyl group in said structural formula (1), a hydroxymethyl group, a hydroxyethyl group, or a hydroxypropyl group is mentioned, and, as for said alkoxyalkyl group, a methoxymethyl group, an ethoxymethyl group, and a methoxy propyl group are mentioned.

[0019]

Also in such an allyl compound (A), especially An allyl chloride, an allyl flora -- heavy current child suction nature group content allyl compound; allyl alcohol, such as ide and an allylcyanide,. Allyl thiol, 2-butene-1, 4-diol, aryloxymethyl 3-ethyl OKISETA nil ether, Glycidyl allyl ether, pentaerythritol monoallyl ether, Polyethylene-glycol monoallyl ether, trimethylolpropane monoallyl ether, Which weak-electric-current child suction nature group content mono-allyl compound; Diaryl ether, Polyethylene-glycol diaryl ether, trimethylolpropane diaryl ether, Weak-electric-current child suction nature group content diaryl compounds, such as pentaerythritol diaryl ether and butane-1,4-diaryl ether; Trimethylolpropane triaryl ether, Weak-electric-current child suction nature group content triaryl compounds, such as pentaerythritol triaryl ether and triallyl cyanurate ether; weak-electric-current child suction nature group content tetra allyl compounds, such as pentaerythritol tetra allyl ether, are preferred.

[0020]

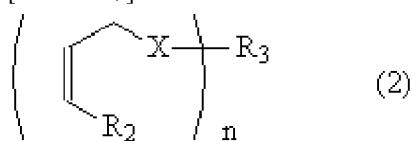
An allyl compound (A) used by this invention has at least one allyl group in the molecular structure as it was described above. However, it is preferred to choose a compound which has two or more allyl groups, such as di-, tri-, and a tetra-allyl compound, from a point that \*\* et al. and the technical effect mentioned above become remarkable. That is, the compound which has two or more allyl groups usually needs to perform a reaction with an alkyl cyclopentadiene dimer (B) by relatively high temperature, and oligomerization of a cyclopentadiene is not usually avoided by it. On the other hand, according to this invention, even if it makes it react under high temperature service temporarily, oligomerization of a cyclopentadiene can be prevented effectively. Di-, a tree, and a tetra-allyl compound which were especially described above also in these compounds from such a viewpoint are preferred.

[0021]

That it can react about said allyl compound (A) even if it is a case where a metaphor allyl group has combined with a weak electron withdrawing group is a point which should be mentioned especially. That is, case [ whose allyl group is / like a compound combined with a weak-electric-current child suction nature functional group ], in order to improve reactivity, a temperature rise of reaction temperature is not avoided. On the other hand, according to this invention, even if it is a case where high temperature service is adopted, generation of oligomer can be effectively controlled, as described above. This viewpoint to said compound (A) has a preferred compound expressed with the following structural formula (2).

[0022]

[Formula 3]



As for  $R_2$ , a hydrogen atom, an alkyl group, a hydroxyalkyl group or an alkoxyalkyl group, and X express an oxygen atom or a sulfur atom,  $R_3$  expresses an alkyl group or multivalent alkylene, and n expresses the integer of 1-4 here.

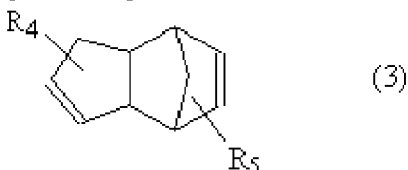
[0023]

Weak-electric-current child suction nature group content mono- \*\* II to which the compound expressed with said structural formula (2) specifically has an oxygen atom or a sulfur atom in the substituent X in said structural formula (2), Tori, and a tetra allyl compound are mentioned.

The alkyl cyclopentadiene dimer (B) used by this invention is the following structural formula (3).

[0024]

[Formula 4]



[0025]

It comes out and what is expressed is mentioned.

[0026]

Here, as for  $R_4$  and  $R_5$ , alkyl groups of C1-C4, such as a methyl group, an ethyl group, a propyl group, and t-butyl group, are mentioned. A point that an effect of this invention is remarkable especially to a methyl-cyclopentadiene is preferred also in these.

[0027]

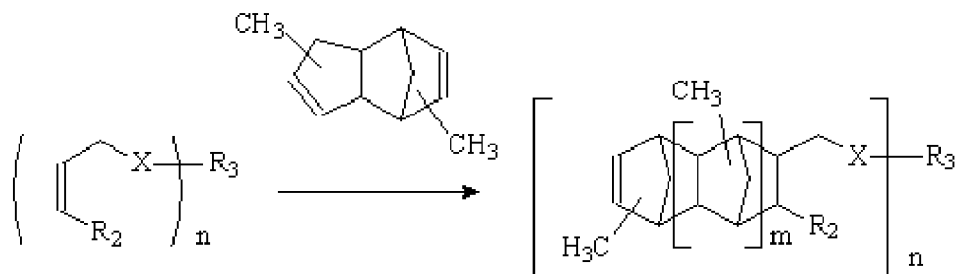
Or generation of a trimer of an alkyl cyclopentadiene or a tetramer is substantially controlled by using an alkyl cyclopentadiene dimer instead of a cyclopentadiene dimer in this invention, generation can be prevented substantially and such an effect is a point which should be mentioned especially. So, for example, a norbornene compound in which it is a high grade and a by-product was reduced can be manufactured by using a methylcyclopentadiene dimer.

[0028]

A reaction of said allyl compound (A) and said alkyl cyclopentadiene dimer (B), Using a compound expressed with a structural formula (2) as this compound (A), as this alkyl cyclopentadiene dimer (B), when using a methylcyclopentadiene dimer, it can express with a following formula.

[0029]

[Formula 5]



[0030]

$X$ ,  $R_2$ ,  $R_3$ , and  $n$  are synonymous with what is defined by said structural formula (2) here, and  $m$  is an integer of 0 or 1.

[0031]

Specifically, a manufacturing method of this invention can be enforced as follows.

First, in the first place, an alkyl cyclopentadiene dimer (B) is mixed with an allyl compound (A) with a room temperature thru/or reaction temperature, or by said temperature conditions, it mixes to an alkyl cyclopentadiene dimer (B), and an allyl compound (A) is ranked second and agitated to it. Here, although reaction temperature can be chosen from the range of 130 °C - 300 °C, when using a compound (A) expressed with said structural formula (2), or when using a compound (A) which has two or more allyl groups, in order to improve reactivity, still higher reaction temperature is chosen. On the other hand, as for this reaction temperature, since oligomerization of an alkyl cyclopentadiene may advance when this reaction temperature is too much high, it is preferred that it is the range of 150-200 °C. Usually, this reaction can be performed under application of pressure. However, when it has °C et al. and the boiling point when especially an allyl compound is lower than 150 °C, or when an allyl compound (B) shows low reactivity, the reaction concerned has especially a preferred thing to perform under a pressure condition in the range of  $1.1 \times 10^5 \text{ Pa}$  -  $1 \times 10^7 \text{ Pa}$ .

[0032]

Equivalent ratio of an allyl group (a) in an allyl compound (A) and a diene group (b) in an alkyl cyclopentadiene dimer (B), Although not restricted, especially when said allyl compound (A) has two or more allyl groups, it is preferred that it is the range of (a):(b) = 1:1 - 1:1.3.

[0033]

An effect that it, on the other hand, controls formation of oligomer of an alkyl cyclopentadiene that it is the range of (a):(b) = 1.1:1 - 2:1 in using one functional compound as an allyl compound (A) is preferred from a remarkable point.

[0034]

In a manufacturing method of this invention, although an organic solvent is not necessarily required, when using it, an inert solvent like xylene or a decalin is preferred.

[0035]

A batch method or a continuous method which used a tubular reactor can perform a manufacturing method of this invention.

While reacting, although a color of a reaction mixture becomes muddy, it can improve by using inactive gas like nitrogen gas.

[0036]

When a reaction is completed, a residual source material is removed by distillation and can be used for the following batch.

[0037]

Output acquired by a manufacturing method of this invention can be refined with a conventional method for those who have the usual knowledge in the technical field concerned.

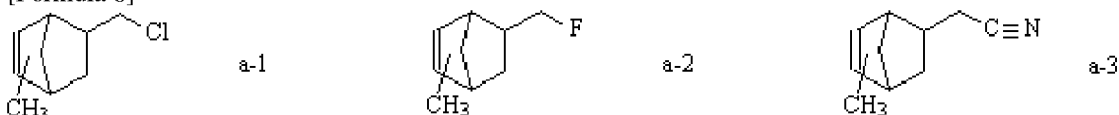
[0038]

Thus, an obtained norbornene derivative can take various structures with those starting materials as it is shown below.

a) Compound which has a heavy current child suction group;

[0039]

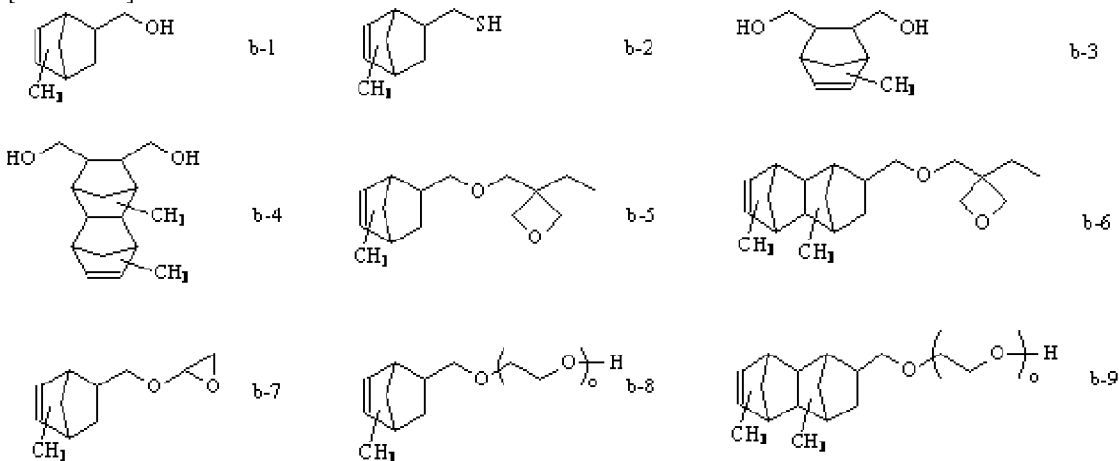
[Formula 6]



b) Compound which has mono- norbornene structure;

[0040]

[Formula 7]



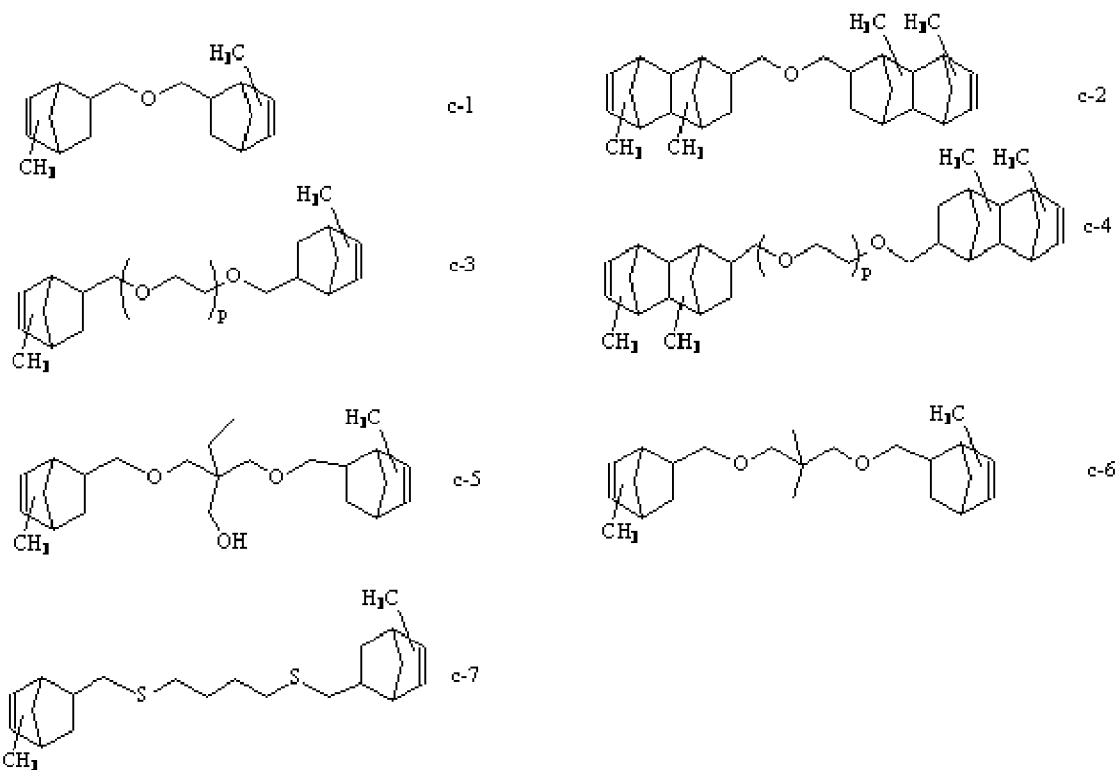
[0041]

As for o, the integer of 1-7 and p express the integer of 1-7 here.

c) Compound which has dinor BORUNEN structure;

[0042]

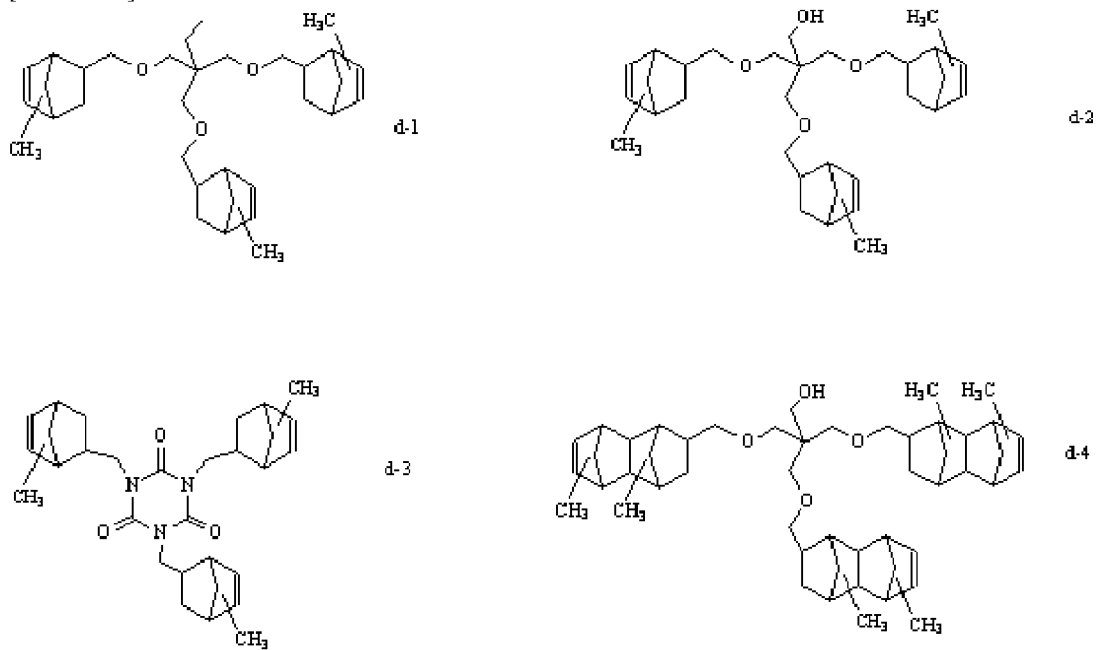
[Formula 8]



d) Compound which has the Tori norbornene structure;

[0043]

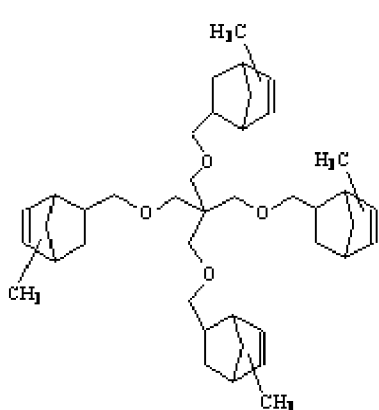
[Formula 9]



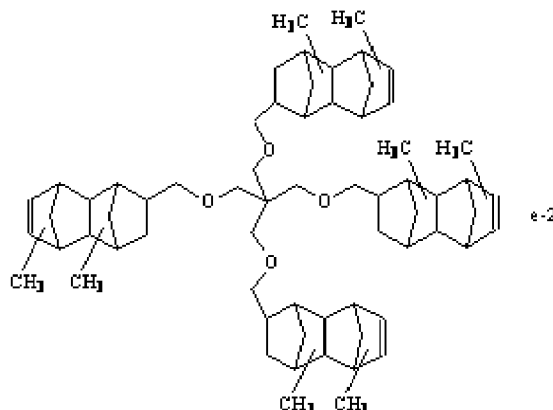
e) Compound which has tetra-norbornene structure;

[0044]

[Formula 10]



e-1



e-2

[0045]

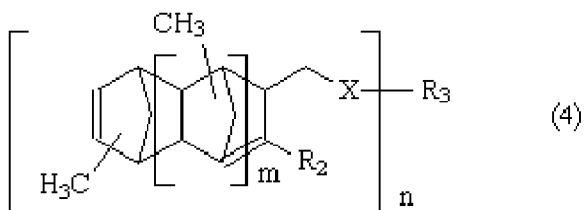
Here, when manufacturing the above-mentioned norbornene derivative, in order that it may generate the isomer which has a methyl group in the position from which norbornene structure differs, the replacement positions of a methyl group are not limited to the above-mentioned structure.

[0046]

When using an allyl compound with a weak-electric-current child suction group as said allyl compound (A) also in these as described above, the norbornene derivative which has the structure especially expressed with the following structural formula (4) from the point that the effect of this invention becomes remarkable is preferred.

[0047]

[Formula 11]



[0048]

X, R<sub>2</sub>, R<sub>3</sub>, and n are synonymous with what is defined by said structural formula (2) among a structural formula (4) here, n is an integer of 1-4 and m is an integer of 0 or 1.

[0049]

The compound which is especially represented by said compounds c-e also in these compounds and which has two or more norbornene structures per monad is useful as a cross linking agent, and preferred from the point of excelling in the reactivity after epoxidating.

[0050]

The compatibility of said unsaturated polyester and styrene is improved by using the compound obtained by this invention as an additive agent for unsaturated polyester, and also hardness and toughness are improved. This compound is useful also as an intermediate at the time of manufacturing an alicyclic epoxy compound.

[Example]

[0051]

Example 1

In the 1-l. 4 mouth flask which has a reflux condenser, an impeller, a thermometer, and a nitrogen feed pipe. 584.0 g (4.0 mol) of 3-aryloxymethyl 3-ethyl OKISETA nil ether and 320.5 g (2.0 mol) of a methylcyclopentadiene dimer were mixed, it ranked second, the inside of a flask was filled with nitrogen gas, and it heated at 170 \*\*.

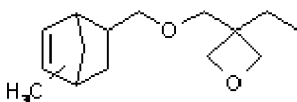
[0052]

After 90% of 3-aryloxymethyl 3-ethyl OKISETA nil ether reacted, where a residual raw material is lightly made decompression (2000-5000 Pa), it distilled off and ranked second, and after cooling to a room temperature, GC-MS analyzed the reaction mixture. The result is as follows.

Output 1:95.2%

[0053]

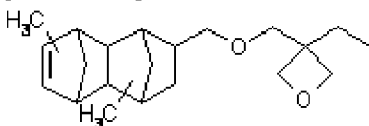
[Formula 12]



Output 2:4.0%

[0054]

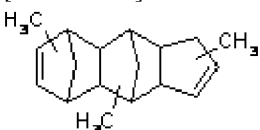
[Formula 13]



By-product: 0.8%

[0055]

[Formula 14]



[0056]

Comparative example 1

In the 1-l. 4 mouth flask which has a reflux condenser, an impeller, a thermometer, and a nitrogen-gas-supplying pipe. 584.0 g (4.0 mol) of 3-aryloxymethyl 3-ethyl OKISETA nil ether and 264.0 g (2.00 mol) of a cyclopentadiene dimer were mixed, it ranked second, the inside of a flask was filled with nitrogen gas, and it heated at 170 \*\*.

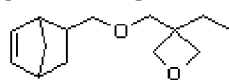
[0057]

After 90% of 3-aryloxymethyl 3-ethyl OKISETA nil ether reacted, where a residual raw material is lightly made decompression (2000-5000 Pa), it distilled off and ranked second, and after cooling to a room temperature, GC-MS analyzed the reaction mixture. The result is as follows.

Output 1:81.3% expressed with the following structural formula

[0058]

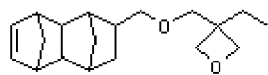
[Formula 15]



Output 2:10.4% expressed with the following structural formula

[0059]

[Formula 16]



The by-product expressed with the following structural formula: 8.3%

[0060]

[Formula 17]



[0061]

Example 2

In the 1-l. 4 mouth flask which has a reflux condenser, an impeller, a thermometer, and a nitrogen-gas-supplying pipe. 317.0 g (1.48 mol) of trimethylolpropane diaryl ether and 238.0 g (1.48 mol) of a methylcyclopentadiene dimer were mixed, it ranked second, the inside of a flask was filled with nitrogen gas, and it heated at 180 \*\*.



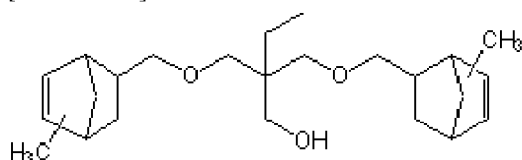
[0062]

After reaching 90% of reaction conversion, by the reduced pressure state (10-100 Pa), the residual raw material was distilled off and it ranked second, and after cooling to a room temperature, GC-MS analyzed the reaction mixture. The result is as follows.

Output 1:89.5% expressed with the following structural formula

[0063]

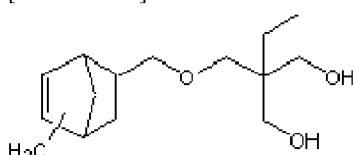
[Formula 18]



Output 2:6.5% expressed with the following structural formula

[0064]

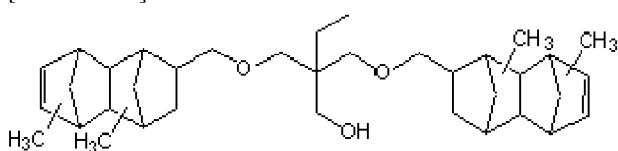
[Formula 19]



Output 3:3.5% expressed with the following structural formula

[0065]

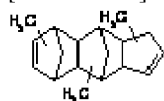
[Formula 20]



By-product 1:0.5% expressed with the following structural formula

[0066]

[Formula 21]



[0067]

Comparative example 2

In the 1-l. 4 mouth flask which has a reflux condenser, an impeller, a thermometer, and a nitrogen-gas-supplying pipe. Trimethylolpropane 535.0 g (2.50 mol) of diaryl ether and 330.5 g (2.50 mol) of a cyclopentadiene dimer were mixed, it ranked second, the inside of a flask was filled with nitrogen gas, and it heated at 180 \*\*.

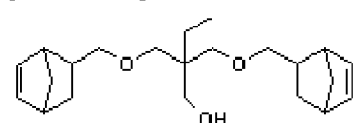
[0068]

After reaching 90% of reaction conversion, by the reduced pressure state (10-100 Pa), the residual raw material was distilled off and it ranked second, and after cooling to a room temperature, GC-MS analyzed the reaction mixture. The result is as follows.

Output 1:80.5% expressed with the following structural formula

[0069]

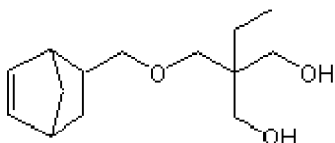
[Formula 22]



Output 2:6.9% expressed with the following structural formula

[0070]

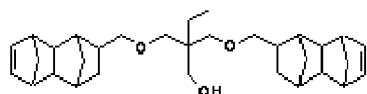
[Formula 23]



Output 3:4.5% expressed with the following structural formula

[0071]

[Formula 24]



By-product 1:8.1% expressed with the following structural formula

[0072]

[Formula 25]



[0073]

Example 3

146.3 g (2.52 mol) of allyl alcohol was taught to autoclave, the inside of this autoclave was decompressed, and it filled with nitrogen gas, and heated at 200 \*\*. Subsequently, 201.6 g (1.26 mol) of a methylenecyclopentadiene dimer was supplied over 2 hours.

After supply is completed, the temperature which is 200 \*\* is held for 1 hour.

Then, it cooled to the room temperature.

Liquid chromatography and a mass spectrum analyzed the reaction mixture.

[0074]

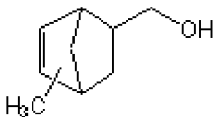
Allyl alcohol: 6.6%

Methylenecyclopentadiene dimer: 2.8%

Methyl-5-norbornene 2-methanol expressed with the following structural formula: 73.5%

[0075]

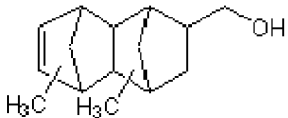
[Formula 26]



JIMECHIRUOKUTAHIDORO dimethanonaphthalene-methanol expressed with the following structural formula: 16.2%

[0076]

[Formula 27]



Methylenecyclopentadiene trimer: 0.8%

Methylenecyclopentadiene tetramer: 0.1%

[0077]

Comparative example 3

146.3 g (2.52 mol) of allyl alcohol was taught to autoclave, the inside of this autoclave was decompressed, and it filled with nitrogen gas, and heated at 200 \*\*. Subsequently, 166.6 g (1.26 mol) of a cyclopentadiene dimer was supplied over 2 hours.

[0078]

After supply is completed, the temperature which is 200 \*\* is held for 1 hour.

Then, it cooled to the room temperature.

Liquid chromatography and a mass spectrum analyzed the obtained reaction mixture.

[0079]

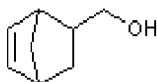
Allyl alcohol: 6.1%

Cyclopentadiene dimer: 1.9%

5-norbornene 2-methanol expressed with the following structural formula: 70.5%

[0080]

[Formula 28]



Octahydro dimethanonaphthalene-methanol expressed with the following structural formula: 13.2%

[0081]

[Formula 29]



[0082]

Cyclopentadiene trimer: 5.3%

Cyclopentadiene tetramer: 3.0%

[0083]

Example 4

100.0 (1.13 mol) of 2-butane-1,4-diol was taught to the flask, the inside was filled with nitrogen gas, and it heated at 195 \*\*. Subsequently, 80.0 g (0.50 mol) of a methylcyclopentadiene dimer was dropped over 5 hours, maintaining 195-200 \*\* temperature conditions to said 2-butane-1,4-diol.

[0084]

After the end of dropping, and also after holding at 200 \*\* for 1 hour, it cooled to the room temperature.

Liquid chromatography and a mass spectrum analyzed the obtained reaction mixture.

[0085]

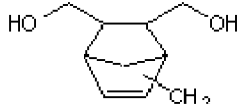
2-butane-1,4-diol: 15.0%

Methylcyclopentadiene dimer: 2.1%

Methyl-5-norbornene 2,3-dimethanol expressed with the following structural formula: 65.5%

[0086]

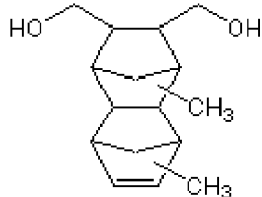
[Formula 30]



Octahydro MECHIRUJIMETANO naphthalene-dimethanol expressed with the following structural formula: 13.8%

[0087]

[Formula 31]



[0088]

Methylcyclopentadiene trimer: 2.3%

Methylcyclopentadiene tetramer: 0.3%

[0089]

Comparative example 4

100.0 (1.13 mol) of 2-butane-1,4-diol was taught to the flask, the inside was filled with nitrogen gas, and

it heated at 195 \*\*. Subsequently, 66.0 g (0.50 mol) of a cyclopentadiene dimer was dropped over 5 hours, maintaining 195-200 \*\* temperature conditions to said 2-butane-1,4-diol.

[0090]

After the end of dropping, and also after holding at 200 \*\* for 1 hour, it cooled to the room temperature. Liquid chromatography and a mass spectrum analyzed the obtained reaction mixture.

[0091]

2-butane-1,4-diol: 16.0%

Cyclopentadiene dimer: 4.1%

5-norbornene 2,3-dimethanol expressed with the following structural formula: 58.5%

[0092]

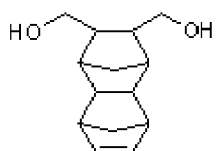
[Formula 32]



Octahydro dimethanonaphthalene-dimethanol expressed with the following structural formula: 12.0%

[0093]

[Formula 33]



[0094]

Cyclopentadiene trimer: 7.1%

Clo pentadiene tetramer: 2.3%

[Translation done.]